

NONPARALLEL SOLUTIONS OF EXTENDED NEMATIC POLYMERS UNDER AN EXTERNAL FIELD

HONG ZHOU

Department of Applied Mathematics
Naval Postgraduate School, Monterey, CA 93943, USA

HONGYUN WANG

Department of Applied Mathematics and Statistics
University of California, Santa Cruz, CA 95064, USA

QI WANG

Department of Mathematics
Florida State University, Tallahassee, FL 32306, USA
and
School of Mathematics, Nankai University
Tianjin, 300071, P. R. China

ABSTRACT. We continue the study on equilibria of the Smoluchowski equation for dilute solutions of rigid extended (dipolar) nematics and dispersions under an imposed electric or magnetic field [25]. We first provide an alternative proof for the theorem that all equilibria are dipolar with the polarity vector parallel to the external field direction if the strength of the permanent dipole (μ) is larger than or equal to the product of the external field (E) and the anisotropy parameter (α_0) (i.e. $\mu \geq |\alpha_0|E$). Then, we show that when $\mu < |\alpha_0|E$, there is a critical value $\alpha^* \geq 1$ for the intermolecular dipole-dipole interaction strength (α) such that all equilibria are either isotropic or parallel to the external field if $\alpha \leq \alpha^*$; but nonparallel dipolar equilibria emerge when $\alpha > \alpha^*$. The nonparallel equilibria are analyzed and the asymptotic behavior of α^* is studied. Finally, the asymptotic results are validated by direct numerical simulations.

1. Introduction. Extended rigid nematic polymers are consisted of dipolar rigid nematic polymers which carry electric dipole or magnetic moments permanently or under an imposed electric or magnetic field [5, 9, 20, 4]. Particle dispersions of electric or magnetic moments in solutions are important materials that have many applications in industries as well [19]. For example, in the manufacture of flexible magnetic data storage media, a fast-moving substrate is coated with one or more layers of dispersions (or inks) composed of sub-micrometer-sized magnetic particles. These magnetic particles are coated with a polymeric binder and dispersed in a solvent. To achieve high data storage capacity, it is very important to control particle orientation in the inks which is sensitive to external aligning fields (flow and magnetic).

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Doi and Edwards used the Doi-Hess kinetic theory to model the homogeneous flows of semi-dilute rodlike nematic polymers that may possess electric dipoles [3, 10, 16]. Recently the Doi-Hess kinetic theory was extended to model magnetic dispersions in viscous solvent [1, 2, 25, 17]. Both theories are essentially identical. Without loss of generality, we focus on the dipolar rigid nematics and magnetic dispersions that are sensitive to magnetic fields. Using a closure approximation a mesoscale constitutive model for magnetic dispersions was developed to study material functions for shear flows and phase transitions at equilibrium [1, 2]. The phase transitions were re-visited by solving the Smoluchowski equation exactly in equilibrium [17]. In this paper we extend our earlier results in [17, 25, 27] to study equilibrium solutions of the Smoluchowski equation, in which the the first moment vector (polarity vector) is not parallel to the external field. We will provide a detailed study on properties of the non-parallel solutions.

The paper is organized as follows. In Section 2 we give a brief description of the properties of magnetic dispersions under an external magnetic field. After reviewing the equilibrium solution of Smoluchowski equation, we prove a series of theorems that characterize the properties of the equilibrium solutions whose polarity vector is not parallel to the external field. The asymptotic result for the critical value of the dipole-dipole interaction strength is derived in Section 3. The details are put in the Appendix. Numerical results are presented in Section 4 to validate the asymptotic results. Finally, in Section 5 we summarize the main results of the paper.

2. Equilibria of Smoluchowski equation for magnetic dispersions or rigid nematic dipolar polymers under an imposed magnetic field. The orientational probability density function for homogeneous flows of magnetic nematic dispersions or rigid nematic polymers $\rho(\mathbf{m}, t)$ is governed by the Smoluchowski equation [25]. It has been shown that the equilibrium solution of the Smoluchowski equation is given by the Boltzmann distribution [6, 7, 8, 12, 21, 22, 26, 11, 25]

$$\rho(\mathbf{m}) = \frac{1}{Z} \exp[-U(\mathbf{m})], \quad Z = \int_S \exp[-U(\mathbf{m})] d\mathbf{m} \quad (1)$$

where \mathbf{m} represents the permanent dipole direction of the nematic molecule in dispersions when $\mu \neq 0$ or the induced dipole direction when $\mu = 0$, $U(\mathbf{m})$ is the total potential energy normalized with respect to kT (k is the Boltzmann constant and T the absolute temperature), Z is the normalizing constant or the total partition function, and S denotes the unit sphere $S = \{\mathbf{m} | \|\mathbf{m}\| = 1\}$.

For dilute solutions of dipolar rigid nematic polymers under an imposed magnetic field (\mathbf{E}), the total potential energy density is given by

$$U(\mathbf{m}) = -\alpha \langle \mathbf{m} \rangle \cdot \mathbf{m} - \mu \mathbf{E} \cdot \mathbf{m} - \frac{\alpha_0}{2} \mathbf{E} \mathbf{E} : \mathbf{m} \mathbf{m}, \quad (2)$$

where α_0 is the difference of the polarizability parallel and perpendicular to \mathbf{m} known as the anisotropy, μ is the strength of the permanent dipole moment, α is the strength of the intermolecular dipole-dipole interaction, $\langle \mathbf{m} \rangle$ is the first moment of the pdf also known as the polarity vector,

$$\langle \mathbf{m} \rangle = \int_S \mathbf{m} \rho(\mathbf{m}) d\mathbf{m}. \quad (3)$$

In this paper, we study dilute nematic polymer solutions or dispersions so the excluded volume effect is neglected in the potential energy. Given the material parameters (α , α_0 , μ , and \mathbf{E}), the potential energy as well as the equilibrium solution

are completely determined by $\langle \mathbf{m} \rangle$ provided the non-linear integral equation for $\langle \mathbf{m} \rangle$ (3) is solved. We shall focus our attention on the solutions of equation (3) for various parameter regimes in this study.

We first establish a coordinate system for \mathbf{m} : we select the z -axis to be the direction of \mathbf{E} , the y -axis to be perpendicular to the plane spanned by $\langle \mathbf{m} \rangle$ and \mathbf{E} ; we also select the positive directions of the x -axis and y -axis such that $\langle \mathbf{m} \rangle$ has a non-negative x -coordinate (if $\langle \mathbf{m} \rangle$ and \mathbf{E} are parallel to each other, then the choice for the x -axis and y -axis is not unique). It is noteworthy that for a given coordinate system with the z -axis parallel to the external field, due to axisymmetry of the problem, if $(r_1, 0, r_3)$ is a solution, then $(r_1 \cos \theta, r_1 \sin \theta, r_3)$ is also a solution for any value of θ . Here we select $(r_1, 0, r_3)$ with $r_1 \geq 0$ to represent this group of solutions.

In this Cartesian coordinate system, we have

$$\begin{aligned} \mathbf{m} &= (m_1, m_2, m_3), \quad \mathbf{E} = E(0, 0, 1), \quad \langle \mathbf{m} \rangle = (r_1, 0, r_3), \quad r_1 \geq 0, \\ U(\mathbf{m}) &= -\alpha r_1 m_1 - (\mu E + \alpha r_3) m_3 - \frac{\alpha_0}{2} E^2 m_3^2. \end{aligned} \quad (4)$$

The nonlinear integral equation (3) becomes

$$\begin{aligned} r_1 &= \int_S m_1 \rho(\mathbf{m}) d\mathbf{m}, \\ 0 &= \int_S m_2 \rho(\mathbf{m}) d\mathbf{m}, \\ r_3 &= \int_S m_3 \rho(\mathbf{m}) d\mathbf{m}. \end{aligned} \quad (5)$$

Note that our choice of the Cartesian coordinate system makes E positive. In this paper we consider the case where $\alpha > 0$, $E > 0$, $|\alpha_0| > 0$ and $\mu > 0$. In [25] we have shown that if $\alpha < 1$, then $\langle \mathbf{m} \rangle$ must be parallel to \mathbf{E} . Furthermore, we have shown that if $\mu \geq |\alpha_0|E$, then $\langle \mathbf{m} \rangle$ must be parallel to \mathbf{E} . In this paper, we will first give an alternative proof for this result based on the torque balance argument and then continue on analyzing the behavior of solutions whose polarity vector is not parallel to the external field direction.

For the theorems below, we introduce a spherical coordinate system in which the y -axis points to the north pole. We use (ψ, ζ) to denote this spherical coordinate system where ψ is the polar angle and ζ is the azimuthal angle. Later on in this paper, we will use another coordinate, which we denote by (ϕ, θ) for distinction, in which the z -axis points to the north pole.

In the (ψ, ζ) spherical coordinate system, we have

$$(m_1, m_2, m_3) = (\sin \psi \sin \zeta, \cos \psi, \sin \psi \cos \zeta), \quad (6)$$

$$U(\psi, \zeta) = U_{Mut}(\psi, \zeta) + U_{Ext}(\psi, \zeta),$$

where the mutual interaction and the external part of the potential are given respectively by

$$\begin{aligned} U_{Mut}(\psi, \zeta) &= -\alpha r_1 \sin \psi \sin \zeta - \alpha r_3 \sin \psi \cos \zeta, \\ U_{Ext}(\psi, \zeta) &= -\mu E \sin \psi \cos \zeta - \frac{\alpha_0}{2} E^2 \sin^2 \psi \cos^2 \zeta. \end{aligned} \quad (7)$$

The equilibrium pdf is given by

$$\rho(\psi, \zeta) = \frac{1}{Z} \exp[-U(\psi, \zeta)], \quad Z = \int_0^\pi \int_{-\pi}^\pi \exp[-U(\psi, \zeta)] d\zeta \sin \psi d\psi. \quad (8)$$

The nonlinear integral equation for r_1 and r_3 becomes

$$\begin{aligned} r_1 &= \int_0^\pi \int_{-\pi}^\pi \sin \psi \sin \zeta \rho(\psi, \zeta) d\psi \sin \psi d\zeta, \\ r_3 &= \int_0^\pi \int_{-\pi}^\pi \sin \psi \cos \zeta \rho(\psi, \zeta) d\psi \sin \psi d\zeta. \end{aligned} \quad (9)$$

Theorem 1. *At equilibrium, the external torque about the y -axis vanishes, i.e.,*

$$\left\langle \frac{\partial}{\partial \zeta} U_{Ext}(\psi, \zeta) \right\rangle = 0. \quad (10)$$

Proof. We first show that

$$\left\langle \frac{\partial}{\partial \zeta} U_{Mut}(\psi, \zeta) + \frac{\partial}{\partial \zeta} U_{Ext}(\psi, \zeta) \right\rangle = 0. \quad (11)$$

Physically, this quantity is the (negative) total torque on the system about the y -axis. Since the system is in equilibrium, the total torque should be zero, i.e.,

$$\begin{aligned} &\left\langle \frac{\partial}{\partial \zeta} U_{Mut}(\psi, \zeta) + \frac{\partial}{\partial \zeta} U_{Ext}(\psi, \zeta) \right\rangle \\ &= -\frac{1}{Z} \int_0^\pi \int_{-\pi}^\pi \frac{\partial}{\partial \zeta} \exp[-U_{Mut}(\psi, \zeta) - U_{Ext}(\psi, \zeta)] d\zeta \sin \psi d\psi = 0. \end{aligned} \quad (12)$$

Next we have that

$$\left\langle \frac{\partial}{\partial \zeta} U_{Mut}(\psi, \zeta) \right\rangle = \langle \alpha r_3 \sin \psi \sin \zeta - \alpha r_1 \sin \psi \cos \zeta \rangle = \alpha r_3 r_1 - \alpha r_1 r_3 = 0, \quad (13)$$

where we have used (9). Equations (12) and (13) lead immediately to (10). We note that (13) is a consequence of the Newton's third law for mutual interaction. \square

Theorem 2. *If $\mu \geq |\alpha_0|E$, then the polarity vector $\langle \mathbf{m} \rangle$ of an equilibrium solution is non-zero and must be parallel to \mathbf{E} .*

Proof. We need to prove that all solutions of (9) satisfy $r_1 = 0$ first. We prove it by contradiction. Suppose there is a solution of (9) satisfying $r_1 > 0$ (recall that the coordinate system is selected to make r_1 non-negative). We are going to show that $\mu \geq |\alpha_0|E$ and $r_1 > 0$ lead to $\left\langle \frac{\partial}{\partial \zeta} U_{Ext}(\psi, \zeta) \right\rangle \neq 0$, which contradicts with (10) proved in Theorem 1 above.

Exploiting the fact that $U_{Ext}(\psi, \zeta)$ is an even function of ζ , we have

$$\begin{aligned} &\left\langle \frac{\partial}{\partial \zeta} U_{Ext}(\psi, \zeta) \right\rangle \\ &= \frac{1}{Z} \int_0^\pi \int_0^\pi \frac{\partial}{\partial \zeta} U_{Ext}(\psi, \zeta) \{ \exp[-U(\psi, \zeta)] - \exp[-U(\psi, -\zeta)] \} d\zeta \sin \psi d\psi. \end{aligned} \quad (14)$$

In the above, the first factor of the integrand satisfies

$$\begin{aligned} \frac{\partial}{\partial \zeta} U_{Ext}(\psi, \zeta) &= \mu E \sin \psi \sin \zeta + \alpha_0 E^2 \sin^2 \psi \cos \zeta \sin \zeta \\ &= (\mu + \alpha_0 E \sin \psi \cos \zeta) E \sin \psi \sin \zeta > 0 \quad \text{for } \zeta \in (0, \pi), \psi \in (0, \pi). \end{aligned} \quad (15)$$

The second factor of the integrand satisfies

$$\begin{aligned} & \exp[-U(\psi, \zeta)] - \exp[-U(\psi, -\zeta)] \\ &= 2\exp\left[\frac{\alpha_0}{2}E^2 \sin^2 \psi \cos^2 \zeta + (\mu E + \alpha r_3) \sin \psi \cos \zeta\right] \sinh(\alpha r_1 \sin \psi \sin \zeta) \quad (16) \\ &> 0 \quad \text{for } \zeta \in (0, \pi), \psi \in (0, \pi). \end{aligned}$$

Substituting (15) and (16) into (14) we obtain $\left\langle \frac{\partial}{\partial \zeta} U_{Ext}(\psi, \zeta) \right\rangle > 0$, which contradicts with (10). Therefore, when $\mu \geq |\alpha_0|E$, $\langle \mathbf{m} \rangle$ must be parallel to \mathbf{E} . \square

Next, we have to show that the polarity vector is not a zero vector, i.e., $r_3 \neq 0$. It follows from (9) that

$$\begin{aligned} r_3 &= \langle \sin \psi \cos \xi \rangle \\ &= \frac{4}{Z} \int_0^{\pi/2} \int_0^{\pi/2} \sin^2 \psi \cos \zeta \sinh((\alpha r_3 + \mu E) \sin \psi \cos \zeta) e^{\frac{\alpha_0}{2}E^2 \sin^2 \psi \cos^2 \zeta} d\psi d\zeta. \end{aligned} \quad (17)$$

This implies that $r_3 \neq 0$ since $r_3 = 0$ contradicts to the above equation.

Now let's look at the intuitive physical picture of the non-parallel solution. Each polymer is subject to two potentials: i) the external potential caused by the magnetic field and ii) the mutual interaction potential caused by the mean field. The net torque effect of the mutual interaction potential is zero by Newton's third law. Therefore, it's the torque due to external field that affects the mesoscale orientation. In addition, it has been shown that a dipolar nematic phase forms beyond $\alpha_c = 3$ when the material is absent of any external field. In the spherical coordinate system where *the pole is on the z-axis*, the external potential is given by

$$U_{Ext}(\phi, \theta) = -\mu E \cos \phi - \frac{\alpha_0}{2} E^2 \cos^2 \phi = -\alpha_0 E^2 \left(\frac{\mu}{\alpha_0 E} \cos \phi + \frac{1}{2} \cos^2 \phi \right),$$

which has two stationary points $\phi = 0$ and $\phi = \pi$ when $\mu \geq |\alpha_0|E$. When $\mu < |\alpha_0|E$, however, the external potential has a third stationary point, ϕ_0 , given by

$$\cos(\phi_0) = -\frac{\mu}{\alpha_0 E}.$$

The torque due to external potential vanishes at the stationary point, leaving the possibility for a nonparallel equilibrium at $\mu < |\alpha_0|E$ and α large enough.

A necessary condition for the existence of the non-parallel solution indicated in Theorem 2 above, $\mu < |\alpha_0|E$, seems to suggest that for large external field (\mathbf{E}), the non-parallel solution shall always exist. However, the theorem below (Theorem 3) tells us that when $\alpha_0 > 0$, non-parallel solution does not exist for large external field. This is physically reasonable. When $\alpha_0 > 0$, the effect of the external field both directly on permanent dipole and indirectly on the polarized dipole tends to align nematic polymers with the external field (parallel and anti-parallel). As one will see, Theorem 3 below does not exclude the existence of non-parallel solution for large external field when $\alpha_0 < 0$. Our numerical simulations show that when $\alpha_0 < 0$, non-parallel solution always exists for large external field. When $\alpha_0 < 0$, the effect of the external field on the polarized dipole tends to align polymer rods perpendicular to the external field, which is what we observe in the numerical simulations.

Theorem 3. *If (r_1, r_3) is a solution of (9) with $r_1 > 0$, then $\alpha_0(\mu E + \alpha r_3) \leq 0$.*

Proof. We prove the theorem by contradiction. Suppose there is a solution of (9) satisfying $r_1 > 0$ and $\alpha_0(\mu E + \alpha r_3) > 0$. We will show that $r_1 > 0$ and $\alpha_0(\mu E + \alpha r_3) > 0$ lead to $\left\langle \frac{\partial}{\partial \zeta} U_{Ext}(\psi, \zeta) \right\rangle > 0$, which contradicts with (10) in Theorem 1.

First we have

$$\begin{aligned} \frac{\partial}{\partial \zeta} U_{Ext}(\psi, \zeta) &= \mu E \sin \psi \sin \zeta + \alpha_0 E^2 \sin^2 \psi \cos \zeta \sin \zeta \\ &\geq \alpha_0 E^2 \sin^2 \psi \cos \zeta \sin \zeta \quad \text{for } \zeta \in (0, \pi), \psi \in (0, \pi). \end{aligned}$$

Substituting it into (14) and using (16), we obtain

$$\begin{aligned} \left\langle \frac{\partial}{\partial \zeta} U_{Ext}(\psi, \zeta) \right\rangle &\geq \frac{1}{Z} \times \\ &\int_0^\pi \int_0^\pi \alpha_0 E^2 \sin^2 \psi \cos \zeta \sin \zeta \{ \exp[-U(\psi, \zeta)] - \exp[-U(\psi, -\zeta)] \} d\zeta \sin \psi d\psi \quad (18) \\ &= \frac{1}{Z} \int_0^\pi \int_0^{\pi/2} 4E^2 \sin^2 \psi \cos \zeta \sin \zeta \exp \left[\frac{\alpha_0}{2} E^2 \sin^2 \psi \cos^2 \zeta \right] g(\psi, \zeta) d\zeta \sin \psi d\psi, \end{aligned}$$

where

$$\begin{aligned} g(\psi, \zeta) &= \alpha_0 \sinh[(\mu E + \alpha r_3) \sin \psi \cos \zeta] \sinh(\alpha r_1 \sin \psi \sin \zeta) \\ &> 0 \quad \text{for } \zeta \in (0, \pi/2), \psi \in (0, \pi), \alpha_0(\mu E + \alpha r_3) > 0. \end{aligned}$$

Thus, we have $\left\langle \frac{\partial}{\partial \zeta} U_{Ext}(\psi, \zeta) \right\rangle > 0$, which contradicts with (10). \square

In [25] we conjectured and numerically confirmed the existence of non-parallel solutions. In the theorem below we give a rigorous proof for the existence of non-parallel solutions.

Theorem 4 (Existence of non-parallel solutions). *For $\mu < |\alpha_0|E$, there exists an $\hat{\alpha}$ (depending on μ , α_0 , and E) such that when $\alpha > \hat{\alpha}$ there is a solution of (9) satisfying $r_1 > 0$.*

Proof. Consider the free energy density

$$F(\alpha, r_3, r_1) = \log \left(\int_0^\pi \int_{-\pi}^\pi \exp[-U(\psi, \zeta)] d\zeta \sin \psi d\psi \right) - \frac{\alpha}{2} (r_1^2 + r_3^2). \quad (19)$$

Equation (9) is equivalent to the Euler-Lagrange equation derived from the free energy density:

$$\frac{\partial}{\partial r_3} F(\alpha, r_3, r_1) = 0, \quad \frac{\partial}{\partial r_1} F(\alpha, r_3, r_1) = 0. \quad (20)$$

We express r_3 and r_1 in polar coordinates

$$r_3 = r \cos \omega, \quad r_1 = r \sin \omega. \quad (21)$$

The function $F(\alpha, r_3, r_1)$ becomes

$$\begin{aligned} & F(\alpha, r, \omega) \\ &= \log \left(\int_0^\pi \int_{-\pi}^\pi \exp[\alpha r \sin \psi \cos(\zeta - \omega) - U_{Ext}(\psi, \zeta)] d\zeta \sin \psi d\psi \right) - \frac{\alpha}{2} r^2 \\ &= \log \left(\int_0^\pi \int_{-\pi}^\pi \exp[\alpha r \sin \psi \cos(\zeta) - U_{Ext}(\psi, \zeta + \omega)] d\zeta \sin \psi d\psi \right) - \frac{\alpha}{2} r^2. \end{aligned} \quad (22)$$

Equation (9) is equivalent to

$$\frac{\partial}{\partial r} F(\alpha, r, \omega) = 0, \quad \frac{\partial}{\partial \omega} F(\alpha, r, \omega) = 0. \quad (23)$$

So we only need to show that for $\mu < |\alpha_0|E$, there exists an $\hat{\alpha}$ (depending on μ , α_0 and E) such that when $\alpha > \hat{\alpha}$ there is a solution of (23) satisfying $r_1 > 0$. We prove it in several steps.

Step 1: Consider the function

$$T_1(\lambda, \omega) = \frac{\int_0^\pi \int_{-\pi}^\pi \exp[\lambda \sin \psi \cos \zeta - U_{Ext}(\psi, \zeta + \omega)] d\zeta \sin \psi d\psi}{\int_0^\pi \int_{-\pi}^\pi \exp[\lambda \sin \psi \cos \zeta] d\zeta \sin \psi d\psi}.$$

We have

$$\lim_{\lambda \rightarrow \infty} T_1(\lambda, \omega) = \exp[-U_{Ext}(\frac{\pi}{2}, \omega)] \equiv T_2(\omega).$$

and the convergence is uniform in ω . The uniform convergence is needed in Step 5 below. We prove this result using the (ε, Λ) notations in Calculus. Note the ε used in this step should not be confused with the ε used in the later part of the paper. For any $\varepsilon > 0$, we want to show that there exists Λ such that $\lambda > \Lambda$ implies

$$|T_1(\lambda, \omega) - T_2(\omega)| < \varepsilon, \quad (24)$$

for all $\omega \in [-\pi, \pi]$. We prove (24) in several substeps.

Substep 1A: We notice that $U_{Ext}(\psi, \zeta)$, $\frac{\partial}{\partial \psi} U_{Ext}(\psi, \zeta)$ and $\frac{\partial}{\partial \zeta} U_{Ext}(\psi, \zeta)$ are bounded for all ψ and ζ . That is, there exists M such that

$$|U_{Ext}(\psi, \zeta)| \leq M, \quad \left| \frac{\partial}{\partial \psi} U_{Ext}(\psi, \zeta) \right| \leq M, \quad \left| \frac{\partial}{\partial \zeta} U_{Ext}(\psi, \zeta) \right| \leq M, \quad (25)$$

for all ψ and ζ . It follows that there exists $0 < \delta < \frac{\pi}{4}$ such that $|\psi - \frac{\pi}{2}| < \delta$ and $|\zeta| < \delta$ implies

$$|\exp(-U_{Ext}(\psi, \zeta + \omega)) - \exp[-U_{Ext}(\frac{\pi}{2}, \omega)]| \leq \frac{1}{4}\varepsilon, \quad (26)$$

for all ω .

Substep 1B: Let us introduce two shorthand notations for the integration domains.

$$\begin{aligned} D &= \left\{ (\psi, \zeta) \mid \left| \psi - \frac{\pi}{2} \right| < \frac{\pi}{2}, |\zeta| < \pi \right\}, \\ D_\delta &= \left\{ (\psi, \zeta) \mid \left| \psi - \frac{\pi}{2} \right| < \delta, |\zeta| < \delta \right\}. \end{aligned}$$

Result (26) leads to

$$\left| \frac{\int_{D_\delta} \exp[\lambda \sin \psi \cos \zeta - U_{Ext}(\psi, \zeta + \omega)] d\zeta \sin \psi d\psi}{\int_{D_\delta} \exp[\lambda \sin \psi \cos \zeta] d\zeta \sin \psi d\psi} - \exp[-U_{Ext}(\frac{\pi}{2}, \omega)] \right| \leq \frac{1}{4}\varepsilon \quad (27)$$

for all ω .

Substep 1C: In $D \setminus D_\delta$, we have either $\cos \zeta \leq \cos \delta$ or $\sin \psi \leq \cos \delta$ or both. It follows that

$$\int_{D \setminus D_\delta} \exp[\lambda \sin \psi \cos \zeta] d\zeta \sin \psi d\psi \leq 2\pi^2 \exp[\lambda \cos \delta] \quad (28)$$

Thus, we have

$$\lim_{\lambda \rightarrow \infty} \lambda \exp(-\lambda) \int_{D \setminus D_\delta} \exp[\lambda \sin \psi \cos \zeta] d\zeta \sin \psi d\psi = 0 \quad (29)$$

In D_δ , using the fact that $\cos z \geq 1 - \frac{z^2}{2}$, and letting $\psi' = \sqrt{\lambda}(\psi - \frac{\pi}{2})$ and $\zeta' = \sqrt{\lambda}\zeta$, we obtain

$$\begin{aligned} & \lambda \exp(-\lambda) \int_{D_\delta} \exp[\lambda \sin \psi \cos \zeta] d\zeta \sin \psi d\psi \\ & \geq \lambda \int_{D_\delta} \exp \left[-\frac{\lambda}{2} \left(\psi - \frac{\pi}{2} \right)^2 - \frac{\lambda}{2} \zeta^2 \right] d\zeta \cos \delta d\psi \\ & = \cos \delta \int_{-\sqrt{\lambda}\delta}^{\sqrt{\lambda}\delta} \int_{-\sqrt{\lambda}\delta}^{\sqrt{\lambda}\delta} \exp \left[\frac{-1}{2} (\psi'^2 + \zeta'^2) \right] d\zeta' d\psi' \\ & \rightarrow 2\pi \cos \delta \quad \text{as } \lambda \rightarrow \infty \end{aligned} \quad (30)$$

Combining (29) and (30) yields

$$\lim_{\lambda \rightarrow \infty} \frac{\int_{D \setminus D_\delta} \exp[\lambda \sin \psi \cos \zeta] d\zeta \sin \psi d\psi}{\int_{D_\delta} \exp[\lambda \sin \psi \cos \zeta] d\zeta \sin \psi d\psi} = 0 \quad (31)$$

Substep 1D: Since $U_{Ext}(\psi, \zeta)$ is bounded, we have

$$\begin{aligned} & \lim_{\lambda \rightarrow \infty} \frac{\int_{D \setminus D_\delta} \exp[\lambda \sin \psi \cos \zeta - U_{Ext}(\psi, \zeta + \omega)] d\zeta \sin \psi d\psi}{\int_{D_\delta} \exp[\lambda \sin \psi \cos \zeta - U_{Ext}(\psi, \zeta + \omega)] d\zeta \sin \psi d\psi} \\ & \leq \exp(2M) \lim_{\lambda \rightarrow \infty} \frac{\int_{D \setminus D_\delta} \exp[\lambda \sin \psi \cos \zeta] d\zeta \sin \psi d\psi}{\int_{D_\delta} \exp[\lambda \sin \psi \cos \zeta] d\zeta \sin \psi d\psi} = 0 \end{aligned} \quad (32)$$

and the convergence is uniform in ω . Combining (31) and (32), we obtain that there exists Λ such that $\lambda > \Lambda$ implies

$$\begin{aligned} & \left| \frac{\int_D e^{[\lambda \sin \psi \cos \zeta - U_{Ext}(\psi, \zeta + \omega)]} d\zeta \sin \psi d\psi}{\int_D e^{[\lambda \sin \psi \cos \zeta]} d\zeta \sin \psi d\psi} \right. \\ & \quad \left. - \frac{\int_{D_\delta} e^{[\lambda \sin \psi \cos \zeta - U_{Ext}(\psi, \zeta + \omega)]} d\zeta \sin \psi d\psi}{\int_{D_\delta} e^{[\lambda \sin \psi \cos \zeta]} d\zeta \sin \psi d\psi} \right| \leq \frac{1}{4}\varepsilon \end{aligned} \quad (33)$$

for all ω . Finally, combining (27) and (33), we conclude that $\lambda > \Lambda$ implies

$$\left| \frac{\int_D e^{[\lambda \sin \psi \cos \zeta - U_{Ext}(\psi, \zeta + \omega)]} d\zeta \sin \psi d\psi}{\int_D e^{[\lambda \sin \psi \cos \zeta]} d\zeta \sin \psi d\psi} - \exp[-U_{Ext}(\frac{\pi}{2}, \omega)] \right| \leq \frac{1}{2}\varepsilon \quad (34)$$

for all ω , which leads immediately to (24).

Step 2: By definition

$$T_2(\omega) = \exp\left[\mu E \cos \omega + \frac{\alpha_0}{2} E^2 \cos^2 \omega\right] \quad (35)$$

Let ω_0 be the angle satisfying $\cos(\omega_0) = \frac{-\mu}{\alpha_0 E}$ and $0 < \omega_0 < \pi$. $T_2(\omega)$ attains a minimum ($\alpha_0 > 0$) or a maximum ($\alpha_0 < 0$) at ω_0 . Below we present the proof for the case of $\alpha_0 > 0$. The case of $\alpha_0 < 0$ can be handled similarly.

We choose $\delta > 0$ such that

$$T_2(\omega_0 - \delta) - T_2(\omega_0) > 0, \quad T_2(\omega_0 + \delta) - T_2(\omega_0) > 0,$$

$$\omega_0 - \delta > 0, \quad \omega_0 + \delta < \pi.$$

Using the result in Step 1, we have

$$\lim_{\lambda \rightarrow \infty} [T_1(\lambda, \omega_0 - \delta) - T_1(\lambda, \omega_0)] > 0, \quad \lim_{\lambda \rightarrow \infty} [T_1(\lambda, \omega_0 + \delta) - T_1(\lambda, \omega_0)] > 0.$$

Step 3: From Step 2, there exists λ_0 such that $\lambda > \lambda_0$ implies

$$T_1(\lambda, \omega_0 - \delta) - T_1(\lambda, \omega_0) > 0, \quad T_1(\lambda, \omega_0 + \delta) - T_1(\lambda, \omega_0) > 0.$$

As a result, for $\lambda > \lambda_0$, $T_1(\lambda, \omega)$, as a function of ω , attains a local minimum in $(\omega_0 - \delta, \omega_0 + \delta)$.

$F(\alpha, r, \omega)$ is related to $T_1(\lambda, \omega)$ as

$$F(\alpha, r, \omega) = \log(T_1(\alpha r, \omega)) + \log\left(\int_0^\pi \int_{-\pi}^\pi \exp[\alpha r \sin \psi \cos \zeta] d\zeta \sin \psi d\psi\right) - \frac{\alpha}{2} r^2.$$

Notice that only the first term depends on ω .

Step 4: From Step 3, we see that when $\alpha > 2\lambda_0$, for each r in $[0.5, 1]$, $F(\alpha, r, \omega)$, as a function of ω , attains a local minimum in $(\omega_0 - \delta, \omega_0 + \delta)$. When $\alpha > 2\lambda_0$, the location of the local minimum defines a function $\omega(r)$ for r in $[0.5, 1]$. $\omega(r)$ satisfies

$$\frac{\partial}{\partial \omega} F(\alpha, r, \omega(r)) = 0, \quad 0 < \omega_0 - \delta < \omega(r) < \omega_0 + \delta < \pi. \quad (36)$$

Step 5: Consider the function

$$T_3(\lambda, \omega) = \frac{\int_0^\pi \int_{-\pi}^\pi \sin \psi \cos \zeta \exp[\lambda \sin \psi \cos \zeta - U_{Ext}(\psi, \zeta + \omega)] d\zeta \sin \psi d\psi}{\int_0^\pi \int_{-\pi}^\pi \exp[\lambda \sin \psi \cos \zeta - U_{Ext}(\psi, \zeta + \omega)] d\zeta \sin \psi d\psi}. \quad (37)$$

We have $T_3(\lambda, \omega) < 1$ for finite λ since $T_3(\lambda, \omega)$ can be viewed as the average of $\sin \psi \cos \zeta$ with respect to a probability density. Furthermore,

$$\lim_{\lambda \rightarrow \infty} T_3(\lambda, \omega) = \sin \frac{\pi}{2} \cos 0 = 1.$$

Since $U_{Ext}(\psi, \zeta)$ is bounded, this convergence is uniform in ω . As a result, there exists λ_1 such that for $\lambda > \lambda_1$ we have

$$\frac{1}{2} < T_3(\lambda, \omega) < 1, \quad \text{for all } \omega.$$

Step 6: Differentiating $F(\alpha, r, \omega)$ with respect to r , we get

$$\frac{\partial}{\partial r} F(\alpha, r, \omega) = \alpha [T_3(\alpha r, \omega) - r].$$

Thus, when $\alpha > 2\lambda_1$, we have

$$\begin{aligned}\frac{\partial}{\partial r}F(\alpha, \frac{1}{2}, \omega) &= \alpha[T_3(\frac{\alpha}{2}, \omega) - \frac{1}{2}] > 0, \\ \frac{\partial}{\partial r}F(\alpha, 1, \omega) &= \alpha[T_3(\alpha, \omega) - 1] < 0.\end{aligned}$$

That means when $\alpha > 2\lambda_1$ for each ω , $\frac{\partial}{\partial r}F(\alpha, r, \omega) = 0$, as an equation for r , has a solution in $[0.5, 1]$. When $\alpha > 2\lambda_1$, the solution defines a function $r(\omega)$ for $\omega \in [0, 2\pi]$. $r(\omega)$ satisfies

$$\frac{\partial}{\partial r}F(\alpha, r(\omega), \omega) = 0, \quad \frac{1}{2} < r(\omega) < 1. \quad (38)$$

Now we combine (36) and (38) to finish the proof. Let $\hat{\alpha} = 2\max(\lambda_0, \lambda_1)$. When $\alpha > \hat{\alpha}$, both (36) and (38) are valid. Let $(r_\alpha, \omega_\alpha)$ be the intersection point of the curve $\omega(r)$ in (36) with curve $r(\omega)$ in (38), as illustrated in Figure 1. At $(r_\alpha, \omega_\alpha)$, We have

$$\begin{aligned}\frac{\partial}{\partial r}F(\alpha, r_\alpha, \omega_\alpha) &= 0, \quad \frac{\partial}{\partial \omega}F(\alpha, r_\alpha, \omega_\alpha) = 0, \\ \frac{1}{2} < r_\alpha < 1, \quad 0 < \omega_\alpha < \pi.\end{aligned}$$

Therefore, $r_3 = r_\alpha \cos \omega_\alpha$, $r_1 = r_\alpha \sin \omega_\alpha$ is a solution of (9) and $r_1 > 0$. This completes the proof of the existence theorem. \square

We just proved that for sufficiently large α non-parallel solution exists. In [25], we showed that for $\alpha < 1$ only parallel solution exists. As we reduce α , the branch of non-parallel solution cannot simply disappear into nowhere. It must be connected to another branch of solution. The non-linear integral equation (9) is symmetric with respect to r_1 . If (r_1, r_3) with $r_1 > 0$ is a solution of (9), then $(-r_1, r_3)$ is also a solution of (9). It is natural to conjecture that as we reduce α the non-parallel solution with $r_1 > 0$ disappears at $\alpha = \alpha^*$ where it is connected to its counterpart (mirror image) with $r_1 < 0$. This conjecture is a reasonable one and it has been confirmed by our extensive numerical simulations (for example, see results in Figure 2). With this conjecture, α^* is the critical value for α such that for $\alpha > \alpha^*$ non-parallel solution exists while for $\alpha \leq \alpha^*$ only parallel solution exists. In this paper, we are going to assume this conjecture is true and we proceed to analyze asymptotic behaviors of the critical value α^* as $\frac{\mu}{|\alpha_0|E} - 1 \rightarrow 0$.

Theorem 5 below identifies the equation for α^* , the intersection point of the non-parallel solution ($r_1 > 0$) with the horizontal line $r_1 = 0$. Then in the next section, we do asymptotic analysis.

Theorem 5. *Suppose a non-parallel solution ($r_1 > 0$) of (5) connects to a parallel solution ($r_1 = 0$) at α^* and r_3^* . Then α^* and r_3^* satisfy*

$$\langle m_3 \rangle|_{r_1=0} = r_3^*, \quad \langle m_1^2 \rangle|_{r_1=0} = \frac{1}{\alpha^*}. \quad (39)$$

Proof. We begin with the fact that α , r_1 and r_3 satisfy system (5). Evaluating the third equation in (5) at $r_1 = 0$, α^* and r_3^* , we get

$$\langle m_3 \rangle|_{r_1=0} = r_3^*.$$

Differentiating the probability density function with respect to $s = \alpha r_1$, we have

$$\begin{aligned}\frac{\partial}{\partial s}\rho(\mathbf{m}) &= \frac{\partial}{\partial s}\left(\frac{1}{Z}\exp[-U(\mathbf{m})]\right) \\ &= \frac{-1}{Z^2}\int_S m_1 \exp[-U(\mathbf{m})]d\mathbf{m} \cdot \exp[-U(\mathbf{m})] + \frac{1}{Z}m_1 \exp[-U(\mathbf{m})] \\ &= -\langle m_1 \rangle \rho(\mathbf{m}) + m_1 \rho(\mathbf{m}).\end{aligned}\quad (40)$$

At the intersection point, $\alpha(r_1)|_{r_1=0} = \alpha^*$ and $s|_{r_1=0} = 0$. Using the definition to calculate the derivative, we obtain

$$\left.\frac{\partial r_1}{\partial s}\right|_{r_1=0} = \lim_{r_1 \rightarrow 0} \frac{r_1 - 0}{\alpha(r_1)r_1 - 0} = \lim_{r_1 \rightarrow 0} \frac{1}{\alpha(r_1)} = \frac{1}{\alpha^*}.\quad (41)$$

Here by introducing variable $s = \alpha r_1$ and using the definition to calculate the derivative $\partial r_1 / \partial s|_{r_1=0}$ directly, we avoid the assumption that the non-parallel branch of $r_1 > 0$ and the non-parallel branch of $r_1 < 0$ are connected smoothly at $r_1 = 0$.

Differentiating the first equation in (5) with respect to $s = \alpha r_1$ and using (40) yields

$$\frac{\partial r_1}{\partial s} = -\langle m_1 \rangle^2 + \langle m_1^2 \rangle \quad (42)$$

Evaluating it at $r_1 = 0$, using (41) and $\langle m_1 \rangle|_{r_1=0} = 0$, we arrive at

$$\langle m_1^2 \rangle|_{r_1=0} = \frac{1}{\alpha^*}.$$

We remark that $\alpha^* \geq 1$ is a direct consequence of the above formula. \square

3. Asymptotic behavior of the critical value α^* . In order to study the behavior of α^* , the critical value of the intermolecular dipole-dipole interaction strength, we switch to the spherical coordinate system (ϕ, θ) where the pole is on the z -axis. In the spherical coordinate system (ϕ, θ) , we have

$$(m_1, m_2, m_3) = (\sin \phi \cos \theta, \sin \phi \sin \theta, \cos \phi),$$

$$U(\phi, \theta) \equiv U_{Mut}(\phi, \theta) + U_{Ext}(\phi, \theta),$$

where the mutual interaction and the external part of the potential are given respectively by

$$U_{Mut}(\phi, \theta) = -\alpha r_1 \sin \phi \cos \theta - \alpha r_3 \cos \phi,$$

$$U_{Ext}(\phi, \theta) = -\mu E \cos \phi - \frac{\alpha_0}{2} E^2 \cos^2 \phi.$$

The steady state probability density is

$$\rho(\phi, \theta) = \frac{1}{Z} \exp[-U(\phi, \theta)], \quad Z = \int_0^\pi \int_{-\pi}^\pi \exp[-U(\phi, \theta)] d\theta \sin \phi d\phi$$

Lemma 1. *In the spherical coordinate system (ϕ, θ) , equation (39) becomes*

$$\begin{aligned} & \frac{\int_{-1}^1 u \exp \left[(\mu E + \alpha^* r_3^*) u + \frac{\alpha_0}{2} E^2 u^2 \right] du}{\int_{-1}^1 \exp \left[(\mu E + \alpha^* r_3^*) u + \frac{\alpha_0}{2} E^2 u^2 \right] du} = r_3^* \\ & \frac{\int_{-1}^1 (1 - u^2) \exp \left[(\mu E + \alpha^* r_3^*) u + \frac{\alpha_0}{2} E^2 u^2 \right] du}{2 \int_{-1}^1 \exp \left[(\mu E + \alpha^* r_3^*) u + \frac{\alpha_0}{2} E^2 u^2 \right] du} = \frac{1}{\alpha^*} \end{aligned} \quad (43)$$

Proof. In the spherical coordinate system (ϕ, θ) , we introduce substitution $u = \cos \phi$. Then, we have

$$\begin{aligned} Z &= \int_0^\pi \int_0^{2\pi} \exp \left[(\mu E + \alpha^* r_3^*) \cos \phi + \frac{\alpha_0}{2} E^2 \cos^2 \phi \right] d\theta \sin \phi d\phi \\ &= 2\pi \int_{-1}^1 \exp \left[(\mu E + \alpha^* r_3^*) u + \frac{\alpha_0}{2} E^2 u^2 \right] du, \\ Z \langle m_3 \rangle &= \int_0^\pi \int_0^{2\pi} \cos \phi \exp \left[(\mu E + \alpha^* r_3^*) \cos \phi + \frac{\alpha_0}{2} E^2 \cos^2 \phi \right] d\theta \sin \phi d\phi \\ &= 2\pi \int_{-1}^1 u \exp \left[(\mu E + \alpha^* r_3^*) u + \frac{\alpha_0}{2} E^2 u^2 \right] du, \\ Z \langle m_1^2 \rangle &= \int_0^\pi \int_0^{2\pi} \sin^2 \phi \cos^2 \theta \exp \left[(\mu E + \alpha^* r_3^*) \cos \phi + \frac{\alpha_0}{2} E^2 \cos^2 \phi \right] d\theta \sin \phi d\phi \\ &= \pi \int_{-1}^1 (1 - u^2) \exp \left[(\mu E + \alpha^* r_3^*) u + \frac{\alpha_0}{2} E^2 u^2 \right] du. \end{aligned}$$

Substituting these into (39), we obtain (43). \square

We consider the case where α_0 and E are fixed while $(|\alpha_0|E - \mu) \rightarrow 0$.

Lemma 2. (A) *When $\alpha_0 > 0$, we have*

$$\lim_{\mu \rightarrow \alpha_0 E} -\alpha^*(\mu) r_3^*(\mu) = \infty. \quad (44)$$

(B) *When $\alpha_0 < 0$, we have*

$$\lim_{\mu \rightarrow (-\alpha_0)E} \alpha^*(\mu) r_3^*(\mu) = \infty. \quad (45)$$

Proof. We prove (A) by contradiction. (B) can be proved in a similar way. Suppose (44) is not true. Using Theorem 3, we have $-\alpha^*(\mu) r_3^*(\mu) \geq \mu E$. The supposition that (44) is not true implies that there is a *bounded* sequence of $-\alpha^*(\mu) r_3^*(\mu)$ as $\mu \rightarrow \alpha_0 E$. Note that $-1 \leq -r_3^*(\mu) \leq 1$ is also bounded. As a result, there is a subsequence $\{\mu_n\}$ satisfying

$$\begin{aligned} \lim_{n \rightarrow \infty} \mu_n &= \alpha_0 E, \\ \lim_{n \rightarrow \infty} -\alpha^*(\mu_n) r_3^*(\mu_n) &= a, \\ \lim_{n \rightarrow \infty} -r_3^*(\mu_n) &= b, \end{aligned} \quad (46)$$

where both a and b are finite: $-1 \leq b \leq 1$ and $a \geq a_0 = \alpha_0 E^2$. Taking the limit on both sides of (43) yields

$$\frac{\int_{-1}^1 u \exp \left[(a_0 - a)u + \frac{a_0}{2}u^2 \right] du}{\int_{-1}^1 \exp \left[(a_0 - a)u + \frac{a_0}{2}u^2 \right] du} = -b, \quad (47)$$

$$\frac{\int_{-1}^1 (1 - u^2) \exp \left[(a_0 - a)u + \frac{a_0}{2}u^2 \right] du}{\int_{-1}^1 \exp \left[(a_0 - a)u + \frac{a_0}{2}u^2 \right] du} = \frac{2b}{a}. \quad (48)$$

Notice that (47) and (48) can be rewritten as

$$\langle u \rangle = -b, \quad \langle 1 - u^2 \rangle = \frac{2b}{a}, \quad (49)$$

where the average is taken with respect to the probability density

$$\rho(u) = \frac{1}{Z} \exp \left[(a_0 - a)u + \frac{a_0}{2}u^2 \right], \quad Z = \int_{-1}^1 \exp \left[(a_0 - a)u + \frac{a_0}{2}u^2 \right] du.$$

We consider the quantity

$$\begin{aligned} & \langle (1 - u^2)[(a_0 - a) + a_0 u] \rangle \\ &= \frac{1}{Z} \int_{-1}^1 (1 - u^2)[(a_0 - a) + a_0 u] \exp \left[(a_0 - a)u + \frac{a_0}{2}u^2 \right] du \\ &= \frac{1}{Z} \int_{-1}^1 (1 - u^2) d \left\{ \exp \left[(a_0 - a)u + \frac{a_0}{2}u^2 \right] \right\} \\ &= \frac{2}{Z} \int_{-1}^1 u \exp \left[(a_0 - a)u + \frac{a_0}{2}u^2 \right] du = 2\langle u \rangle. \end{aligned}$$

From (49), we have

$$\begin{aligned} \langle (1 - u^2)u \rangle &= \frac{1}{a_0} [\langle (1 - u^2)[(a_0 - a) + a_0 u] \rangle - \langle 1 - u^2 \rangle(a_0 - a)] \\ &= \frac{1}{a_0} [2\langle u \rangle - \langle 1 - u^2 \rangle(a_0 - a)] = \frac{1}{a_0} \left[-2b - \frac{2b}{a}(a_0 - a) \right] = -\frac{2b}{a}. \end{aligned}$$

Combining this result with (49), we obtain

$$\langle (1 - u^2)(1 + u) \rangle = \langle 1 - u^2 \rangle + \langle (1 - u^2)u \rangle = \frac{2b}{a} - \frac{2b}{a} = 0. \quad (50)$$

On the other hand,

$$\langle (1 - u^2)(1 + u) \rangle = \int_{-1}^1 (1 - u^2)(1 + u)\rho(u)du > 0. \quad (51)$$

(50) contradicts with (51). Therefore, $\lim_{\mu \rightarrow \alpha_0 E} -\alpha^*(\mu)r_3^*(\mu) = \infty$. \square

Now we introduce another Lemma based on Laplace's method before deriving the asymptotic behavior for α^* .

Lemma 3. *Suppose $f(u)$ is a quadratic function satisfying $f(-1) = 0$ and $g(u)$ is a quadratic function. As $\lambda \rightarrow \infty$, we have*

$$\begin{aligned} I(\lambda) &\equiv \frac{\int_{-1}^1 f(u) \exp[-\lambda u + g(u)] du}{\int_{-1}^1 \exp[-\lambda u + g(u)] du} \\ &= \frac{f' \frac{1}{\lambda} + (2f'g' + f'') \frac{1}{\lambda^2} + [3(g'' + g'^2)f' + 3f''g'] \frac{1}{\lambda^3} + \cdots}{1 + g' \frac{1}{\lambda} + (g'' + g'^2) \frac{1}{\lambda^2} + \cdots}, \end{aligned} \quad (52)$$

where all the derivatives are evaluated at -1 .

Proof. Using the substitution $u = -1 + \frac{v}{\lambda}$, we have

$$I(\lambda) = \frac{\int_0^{2\lambda} f(-1 + \frac{v}{\lambda}) \exp[g(-1 + \frac{v}{\lambda})] \exp(-v) dv}{\int_0^{2\lambda} \exp[g(-1 + \frac{v}{\lambda})] \exp(-v) dv}.$$

Expanding functions f and g , we obtain

$$\begin{aligned} I(\lambda) &= \frac{\int_0^{2\lambda} \left[f'(-1) \frac{v}{\lambda} + \frac{f''(-1)}{2} \frac{v^2}{\lambda^2} \right] \exp \left[g'(-1) \frac{v}{\lambda} + \frac{g''(-1)}{2} \frac{v^2}{\lambda^2} \right] \exp(-v) dv}{\int_0^{2\lambda} \exp \left[g'(-1) \frac{v}{\lambda} + \frac{g''(-1)}{2} \frac{v^2}{\lambda^2} \right] \exp(-v) dv} \\ &= \frac{\int_0^{2\lambda} f' \frac{v}{\lambda} \left[1 + \frac{f''}{2f'} \frac{v}{\lambda} \right] \cdot \left[1 + g' \frac{v}{\lambda} + \left(\frac{g'' + g'^2}{2} \right) \frac{v^2}{\lambda^2} + \cdots \right] \exp(-v) dv}{\int_0^{2\lambda} \left[1 + g' \frac{v}{\lambda} + \left(\frac{g'' + g'^2}{2} \right) \frac{v^2}{\lambda^2} + \cdots \right] \exp(-v) dv} \\ &= \frac{\int_0^{2\lambda} f' \frac{v}{\lambda} \left[1 + \left(g' + \frac{f''}{2f'} \right) \frac{v}{\lambda} + \left(\frac{g'' + g'^2}{2} + \frac{f''}{2f'} g' \right) \frac{v^2}{\lambda^2} + \cdots \right] \exp(-v) dv}{\int_0^{2\lambda} \left[1 + g' \frac{v}{\lambda} + \left(\frac{g'' + g'^2}{2} \right) \frac{v^2}{\lambda^2} + \cdots \right] \exp(-v) dv}, \end{aligned}$$

where all the derivatives are evaluated at -1 . Note that

$$\lim_{\lambda \rightarrow \infty} \int_0^{2\lambda} v^k \exp(-v) dv = \int_0^\infty v^k \exp(-v) dv = k!$$

and the convergence is exponential, the result (52) follows immediately. \square

We now present the main asymptotic results for α^* as $(|\alpha_0|E - \mu) \rightarrow 0$.

Theorem 6. Let $\varepsilon = \frac{|\alpha_0 E| - \mu}{|\alpha_0 E|}$. As $\varepsilon \rightarrow 0$, α^* behaves like

$$\alpha^* = \frac{1}{\varepsilon} \cdot \left[2 + \frac{1}{2}\varepsilon + \left(\frac{1}{2}\alpha_0 E^2 + \frac{1}{8} \right) \varepsilon^2 + \dots \right]. \quad (53)$$

Proof. We present the proof for the case of $\alpha_0 > 0$. The case of $\alpha_0 < 0$ can be proved in a similar way using a lemma similar to Lemma 3.

For the case of $\alpha_0 > 0$, we derive the first term of expansion

$$\alpha^* = \frac{2}{\varepsilon} + \dots \quad (54)$$

It turns out that once we obtain the first term, it helps us simplify significantly the derivation of subsequent terms. The detailed derivation of the three term asymptotic expansion (53) is given in the Appendix.

Let $\lambda = -\alpha^* r_3^*$ and $g(u) = \mu Eu + \frac{\alpha_0}{2} E^2 u^2$. Lemma 2 shows that as $\varepsilon \rightarrow 0$ we have $\lambda \rightarrow \infty$. Applying Lemma 3 to the first equation of (43) with $f(u) = 1 + u$, we have

$$r_3^* + 1 = \frac{\frac{1}{\lambda} + 2g' \frac{1}{\lambda^2} + 3(g'' + g'^2) \frac{1}{\lambda^3} + \dots}{1 + g' \frac{1}{\lambda} + (g'' + g'^2) \frac{1}{\lambda^2} + \dots}. \quad (55)$$

Applying Lemma 3 to the second equation of (43) with $f(u) = 1 - u^2$, we arrive at

$$\frac{-r_3^*}{\lambda} = \frac{\frac{1}{\lambda} + (2g' - 1) \frac{1}{\lambda^2} + [3(g'' + g'^2) - 3g'] \frac{1}{\lambda^3} + \dots}{1 + g' \frac{1}{\lambda} + (g'' + g'^2) \frac{1}{\lambda^2} + \dots}. \quad (56)$$

Solving $(r_3^* + 1)$ from (56) yields

$$r_3^* + 1 = \frac{(1 - g') \frac{1}{\lambda} + [3g' - 2(g'' + g'^2)] \frac{1}{\lambda^2} + \dots}{1 + g' \frac{1}{\lambda} + (g'' + g'^2) \frac{1}{\lambda^2} + \dots}. \quad (57)$$

Equating (55) and (57) gives

$$\frac{1}{\lambda} + 2g' \frac{1}{\lambda^2} + 3(g'' + g'^2) \frac{1}{\lambda^3} + \dots = (1 - g') \frac{1}{\lambda} + [3g' - 2(g'' + g'^2)] \frac{1}{\lambda^2} + \dots,$$

which in turn leads to

$$g' \lambda = [g' - 2(g'' + g'^2)] + \dots \quad (58)$$

Taking derivatives of $g(u) = \mu Eu + \frac{\alpha_0}{2} E^2 u^2$, we have

$$g'(-1) = -(\alpha_0 E^2 - \mu E) = -\alpha_0 E^2 \varepsilon, \quad g''(-1) = \alpha_0 E^2 = O(1).$$

The right hand side of (58) is

$$g' - 2(g'' + g'^2) = -2\alpha_0 E^2 + O(\varepsilon).$$

The left hand side of (58) must match the right hand side. Thus it follows that

$$\lambda = \frac{2}{\varepsilon} + \dots \quad (59)$$

Equation (55) shows that as $\lambda \rightarrow \infty$ we have $r_3^* \rightarrow (-1)$. Therefore, we conclude that

$$\alpha^* = \frac{2}{\varepsilon} + \dots \quad (60)$$

□

Remark: This asymptotic behavior of α^* has been confirmed in our numerical simulations (see next section).

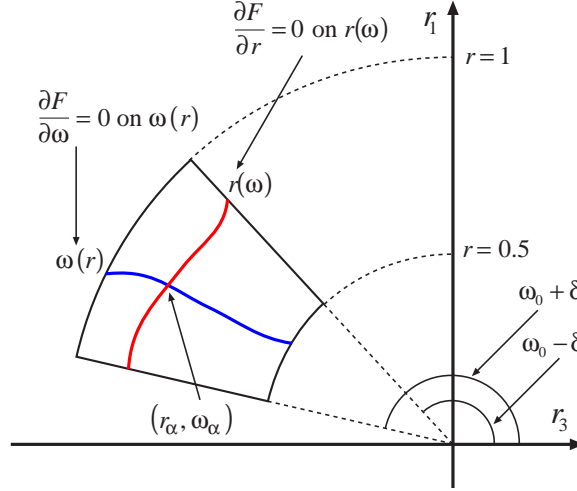


FIGURE 1. Diagram of function $\omega(r)$ and function $r(\omega)$. Along $\omega(r)$, $\partial F/\partial \omega = 0$ and along $r(\omega)$, $\partial F/\partial r = 0$. At the intersection point $(\omega_\alpha, r_\alpha)$, the gradient of F is zero. Hence $(\omega_\alpha, r_\alpha)$ is a solution of equation (23).

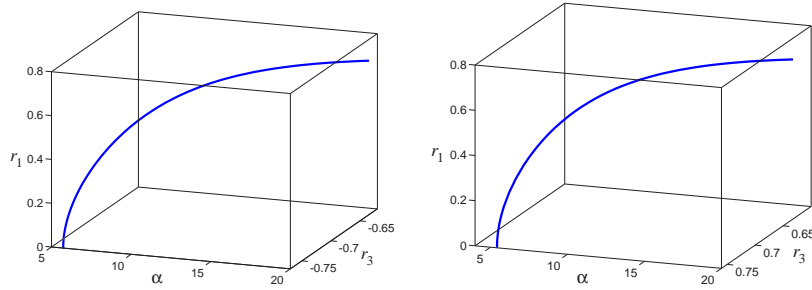


FIGURE 2. The components of the polarity vector r_1 and r_3 as functions of α with respect to $\alpha_0 = 1, -1$. Parameter values used here are: $\mu = 0.6$, $E = 1$, $\alpha \in [5, 20]$. Left panel: $\alpha_0 = 1$. Right panel: $\alpha_0 = -1$.

4. Numerical results. We solve eq. (9) numerically to validate the asymptotic results obtained above. Figure 2 shows nonparallel solutions for the case of $\alpha_0 = 1$ (left panel) and $\alpha_0 = -1$ (right panel). r_1 and r_3 are shown as functions of α . For $\alpha_0 = 1$ (left panel), the critical value is $\alpha^* \approx 5.7227$ and the value of r_3 is

negative. This is consistent with the fact that for $\alpha_0 > 0$ the third stationary point of the external potential is in the same hemisphere as the negative direction of the external field. The parameter values used in simulations are listed in the figure caption. For $\alpha_0 = -1$ (right panel), the critical value is $\alpha^* \approx 5.3835$ and the value of r_3 is positive. This is consistent with the fact that for $\alpha_0 < 0$ the third stationary point of the external potential is in the same hemisphere as the positive direction of the external field. Figure 3 shows r_1 and r_3 as functions of α . For the case of $\alpha_0 = 1$ (left panel), nonparallel solution exists only in a bounded interval of E . The lower limit of E is explained by Theorem 2, which says the necessary condition for the existence of non-parallel solution is $E \geq \frac{\mu}{|\alpha_0|}$. This is only a necessary condition, not sufficient. The actual lower critical value is $E_{lower}^* \approx 0.7619$. The parameter values used in simulations are given in the figure caption. The upper limit of E is explained by Theorem 3, which says for $\alpha_0 > 0$ another necessary condition for the existence of nonparallel solution is $\mu E \leq \alpha(-r_3) \leq \alpha$. Again, this is only a necessary condition, not sufficient. The actual upper critical value is $E_{upper}^* \approx 3.3921$. For the case $\alpha_0 = -1$ (right panel), nonparallel solution exists when E is above a critical value, explained by Theorem 2. For $\alpha_0 < 0$, Theorem 3 does not impose an additional condition for the existence of nonparallel solution.

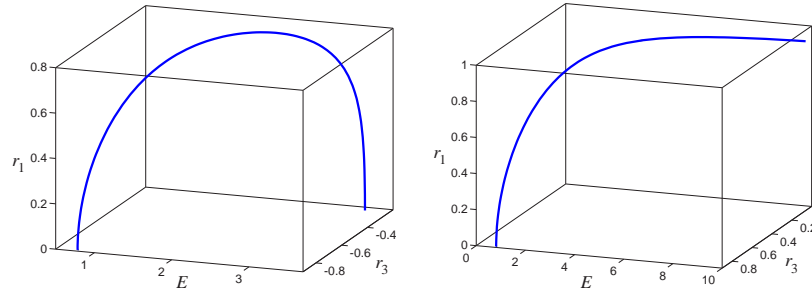


FIGURE 3. The components of the polarity vector r_1 and r_3 as functions of E with respect to $\alpha_0 = 1, -1$. Parameter values used here are: $\mu = 0.6$, $\alpha = 10$, $E \in [0, 10]$. Left panel: $\alpha_0 = 1$. Right panel: $\alpha_0 = -1$.

In order to confirm the asymptotic result (54) for α^* , we compare the asymptotic result from (54) with the direct numerical solution of equation (43). Figure 4 demonstrates that the asymptotic expansion is accurate for both the case of $\alpha_0 = 1$ (left panel) and the case of $\alpha_0 = -1$ (right panel). Figure 5 focuses on the performance of the asymptotic formula for ε near 1 where the asymptotic formula is not expected to yield accurate result. For the case of $\alpha_0 = 1$ (left panel) the asymptotic formula is very good even for ε close to 1. The maximum relative error is less than 3%. For the case of $\alpha_0 = -1$ (right panel) the result of asymptotic formula is still acceptable although for ε near 1 the relative error is about 25%. Finally, Figure 6 shows the absolute error in asymptotic formula (54) as a function of ε . Here the error is defined as the absolute value of the difference between the numerical solution of equation (43) and the asymptotic result (53). As shown in Figure 6, for both the case of $\alpha_0 = 1$ and the case of $\alpha_0 = -1$, the error decays like ε^2 or faster as $\varepsilon \rightarrow 0$.

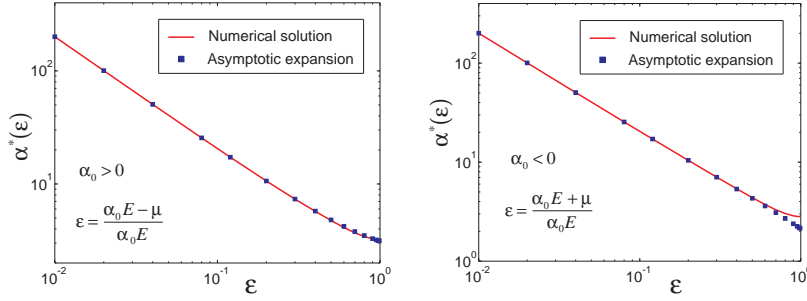


FIGURE 4. Log-log plots of $\alpha^*(\varepsilon)$ as a function of ε . Solid line represents the numerical solution of equation (43). Symbols represent the asymptotic result (53). Left panel: $\alpha_0 = 1$; Right panel: $\alpha_0 = -1$. They demonstrate that the asymptotic expansion is accurate for both the case of $\alpha_0 > 0$ and the case of $\alpha_0 < 0$. Parameter values used here are: $E = 1$, $\mu \in [0.01, 0.99]$.

5. Concluding remarks. In this work we have studied the equilibria of Smoluchowski equation for dilute solutions of dipolar nematic polymers and magnetic dispersions under an imposed external field. We establish the existence of a critical value of the dipole-dipole intermolecular strength above which a class of nonparallel equilibria exists where the polarity vector is not parallel to the direction of the external field. An asymptotic formula for the critical value is established in terms of the other material parameters and compared with direct numerical computations. The rigorous as well as asymptotic results for the equilibria of the Smoluchowski equation will provide valuable insights into the governing system of pdes which is prototypical in kinetic theories for solution of polymers and dispersions [13, 18, 23, 24, 14].

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Appendix. Asymptotic expansion of α^* with more terms

In this appendix, we derive (53). Recall that $\lambda = -\alpha^* r_3^*$ and $g(u) = \mu Eu + \frac{\alpha_0}{2} E^2 u^2$. From the previous analysis in Theorem 5, we know

$$g'(-1) = -(\alpha_0 E^2 - \mu E) = O\left(\frac{1}{\lambda}\right), \quad g''(-1) = \alpha_0 E^2 = O(1).$$

This will be very helpful in simplifying the expansion below.

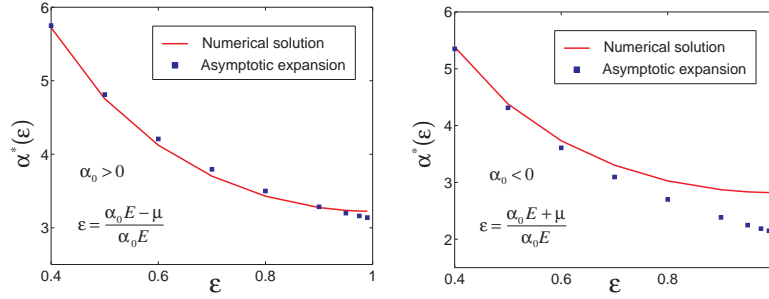


FIGURE 5. Linear plots of $\alpha^*(\varepsilon)$ as a function of ε for ε near 1. Note that the asymptotic formula is derived in the limit of $\varepsilon \rightarrow 0$ and is not supposed to be valid near $\varepsilon = 1$. Solid line represents the numerical solution of equation (43). Symbols represent the asymptotic result (53). Left panel: $\alpha_0 = 1$; Right panel: $\alpha_0 = -1$. In the left panel, it is clear that the asymptotic formula is very good for the case of $\alpha_0 > 0$ even for ε close to 1. Parameter values used here are: $E = 1$, $\mu \in [0.01, 0.99]$.

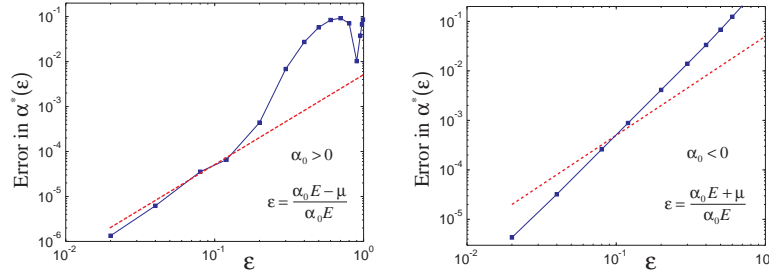


FIGURE 6. Error in $\alpha(\varepsilon)$ as a function of ε . Error is defined as the absolute value of the difference between the numerical solution of equation (43) and the asymptotic result (53). Left panel: $\alpha_0 = 1$; Right panel: $\alpha_0 = -1$. From the figure, we can see that as $\varepsilon \rightarrow 0$, the error decays like ε^2 or faster. The blue line and symbols represent the error. The red dashed line shows $y = c\varepsilon^2$. The red line is drawn to guide your eyes and to show the behavior of error as $\varepsilon \rightarrow 0$. Parameter values used here are: $E = 1$, $\mu \in [0.01, 0.99]$.

Lemma 1A: Suppose $f(u)$ is a quadratic function satisfying $f(-1) = 0$. As $\lambda \rightarrow \infty$, we have

$$\begin{aligned}
 I(\lambda) &= \frac{\int_{-1}^1 f(u) \exp[-\lambda u + g(u)] du}{\int_{-1}^1 \exp[-\lambda u + g(u)] du} \\
 &= \frac{f' \frac{1}{\lambda} + (2f'g' + f'') \frac{1}{\lambda^2} + [3(g'' + g'^2)f' + 3f''g'] \frac{1}{\lambda^3} + [12g'g''f' + 6g''f''] \frac{1}{\lambda^4} + 15g''^2f' \frac{1}{\lambda^5} + \dots}{1 + g' \frac{1}{\lambda} + (g'' + g'^2) \frac{1}{\lambda^2} + 3g'g'' \frac{1}{\lambda^3} + 3g''^2 \frac{1}{\lambda^4} + \dots},
 \end{aligned} \tag{61}$$

where all the derivatives are evaluated at (-1) .

Proof of Lemma 1A: Using the substitution $u = -1 + \frac{v}{\lambda}$, we have

$$I(\lambda) = \frac{\int_0^{2\lambda} f(-1 + \frac{v}{\lambda}) \exp[g(-1 + \frac{v}{\lambda})] \exp(-v) dv}{\int_0^{2\lambda} \exp[g(-1 + \frac{v}{\lambda})] \exp(-v) dv}.$$

f and g , we obtain

$$\begin{aligned} I(\lambda) &= \frac{\int_0^{2\lambda} \left[f'(-1) \frac{v}{\lambda} + \frac{f''(-1)}{2} \frac{v^2}{\lambda^2} \right] \exp \left[g'(-1) \frac{v}{\lambda} + \frac{g''(-1)}{2} \frac{v^2}{\lambda^2} \right] \exp(-v) dv}{\int_0^{2\lambda} \exp \left[g'(-1) \frac{v}{\lambda} + \frac{g''(-1)}{2} \frac{v^2}{\lambda^2} \right] \exp(-v) dv} = \\ &= \frac{\int_0^{2\lambda} f' \frac{v}{\lambda} \left[1 + \frac{f''}{2f'} \frac{v}{\lambda} \right] \cdot \left[1 + g' \frac{v}{\lambda} + \left(\frac{g'' + g'^2}{2} \right) \frac{v^2}{\lambda^2} + \frac{g'g''}{2} \frac{v^3}{\lambda^3} + \frac{g''^2}{8} \frac{v^4}{\lambda^4} + \dots \right] e^{-v} dv}{\int_0^{2\lambda} \left[1 + g' \frac{v}{\lambda} + \left(\frac{g'' + g'^2}{2} \right) \frac{v^2}{\lambda^2} + \frac{g'g''}{2} \frac{v^3}{\lambda^3} + \frac{g''^2}{8} \frac{v^4}{\lambda^4} + \dots \right] \exp(-v) dv} \\ &= \frac{\int_0^{2\lambda} f' \frac{v}{\lambda} \left[1 + \left(g' + \frac{f''}{2f'} \right) \frac{v}{\lambda} + \left(\frac{g'' + g'^2}{2} + \frac{f''}{2f'} g' \right) \frac{v^2}{\lambda^2} + \left(\frac{g'g''}{2} + \frac{g''}{2} \frac{f''}{f'} \right) \frac{v^3}{\lambda^3} + \frac{g''^2}{8} \frac{v^4}{\lambda^4} + \dots \right] e^{-v} dv}{\int_0^{2\lambda} \left[1 + g' \frac{v}{\lambda} + \left(\frac{g'' + g'^2}{2} \right) \frac{v^2}{\lambda^2} + \frac{g'g''}{2} \frac{v^3}{\lambda^3} + \frac{g''^2}{8} \frac{v^4}{\lambda^4} + \dots \right] e^{-v} dv}, \end{aligned}$$

where all the derivatives are evaluated at -1 . In the above expansion, we have used the fact $g' = O\left(\frac{1}{\lambda}\right)$ and omitted terms of the order higher than $1/\lambda^4$. For example, we omitted the term $\frac{g'^3}{6} \frac{v^3}{\lambda^3}$. Using

$$\lim_{\lambda \rightarrow \infty} \int_0^{2\lambda} v^k \exp(-v) dv = \int_0^{\infty} v^k \exp(-v) dv = k!$$

we obtain the result (61). \square

Theorem 1A: Let $\varepsilon = \frac{(\alpha_0 E - \mu)}{\alpha_0 E}$. As $\varepsilon \rightarrow 0$, α^* behaves like

$$\alpha^* = \frac{1}{\varepsilon} \cdot \left[2 + \frac{1}{2} \varepsilon + \left(\frac{1}{2} \alpha_0 E^2 + \frac{1}{8} \right) \varepsilon^2 + \dots \right]. \quad (62)$$

Proof: Applying Lemma 1A to the first equation of (43) with $f(u) = 1 + u$, it follows that

$$r_3^* + 1 = \frac{\frac{1}{\lambda} + 2g' \frac{1}{\lambda^2} + 3(g'' + g'^2) \frac{1}{\lambda^3} + 12g'g'' \frac{1}{\lambda^4} + 15g''^2 \frac{1}{\lambda^5} + \dots}{1 + g' \frac{1}{\lambda} + (g'' + g'^2) \frac{1}{\lambda^2} + 3g'g'' \frac{1}{\lambda^3} + 3g''^2 \frac{1}{\lambda^4} + \dots}. \quad (63)$$

Applying Lemma 1A to the second equation of (43) with $f(u) = 1 - u^2$, one has

$$\frac{-r_3^*}{\lambda} = \frac{\frac{1}{\lambda} + (2g' - 1)\frac{1}{\lambda^2} + [(g'' + g'^2) - g']\frac{3}{\lambda^3} + [12g'g'' - 6g'']\frac{1}{\lambda^4} + g''^2\frac{15}{\lambda^5} + \dots}{1 + g'\frac{1}{\lambda} + (g'' + g'^2)\frac{1}{\lambda^2} + 3g'g''\frac{1}{\lambda^3} + 3g''^2\frac{1}{\lambda^4} + \dots}. \quad (64)$$

Solving $(r_3^* + 1)$ from (64) yields

$$r_3^* + 1 = \frac{(1 - g')\frac{1}{\lambda} + [3g' - 2(g'' + g'^2)]\frac{1}{\lambda^2} + [6g'' - 9g'g'']\frac{1}{\lambda^3} - 12g''^2\frac{1}{\lambda^4} + \dots}{1 + g'\frac{1}{\lambda} + (g'' + g'^2)\frac{1}{\lambda^2} + 3g'g''\frac{1}{\lambda^3} + 3g''^2\frac{1}{\lambda^4} + \dots}. \quad (65)$$

Equating (63) with (65), we have

$$\begin{aligned} & \frac{1}{\lambda} + 2g'\frac{1}{\lambda^2} + 3(g'' + g'^2)\frac{1}{\lambda^3} + 12g'g''\frac{1}{\lambda^4} + 15g''^2\frac{1}{\lambda^5} + \dots \\ &= (1 - g')\frac{1}{\lambda} + [3g' - 2(g'' + g'^2)]\frac{1}{\lambda^2} + [6g'' - 9g'g'']\frac{1}{\lambda^3} - 12g''^2\frac{1}{\lambda^4} + \dots \end{aligned}$$

which leads to

$$g'\lambda = -2g'' + g' - 2g'^2 + [3g'' - 9g'g'']\frac{1}{\lambda} - 12g''^2\frac{1}{\lambda^3} + \dots. \quad (66)$$

Recall $\varepsilon = \frac{(\alpha_0 E - \mu)}{\alpha_0 E}$. Substituting

$$g'(-1) = -\alpha_0 E^2 \varepsilon, \quad g''(-1) = \alpha_0 E^2$$

into (66), we get

$$\begin{aligned} -\alpha_0 E^2 \varepsilon \lambda &= -2\alpha_0 E^2 - \alpha_0 E^2 \varepsilon - 2(\alpha_0 E^2)^2 \varepsilon^2 \\ &+ 3\alpha_0 E^2 (1 + 3\alpha_0 E^2 \varepsilon) \frac{\varepsilon}{\varepsilon \lambda} - 12(\alpha_0 E^2)^2 \frac{\varepsilon^2}{(\varepsilon \lambda)^2} + \dots. \end{aligned} \quad (67)$$

We already know $\varepsilon \lambda = O(1)$. We seek a solution of the form $\varepsilon \lambda = c_0 + c_1 \varepsilon + c_2 \varepsilon^2 + \dots$. Substituting this expansion form in (67), we obtain

$$\begin{aligned} -\alpha_0 E^2 (c_0 + c_1 \varepsilon + c_2 \varepsilon^2) &= -2\alpha_0 E^2 - \alpha_0 E^2 \varepsilon - 2(\alpha_0 E^2)^2 \varepsilon^2 \\ &+ 3\alpha_0 E^2 (1 + 3\alpha_0 E^2 \varepsilon) \frac{\varepsilon}{c_0 + c_1 \varepsilon} - 12(\alpha_0 E^2)^2 \frac{\varepsilon^2}{c_0^2} + \dots. \end{aligned}$$

Equating coefficients of corresponding powers of ε gives

$$\varepsilon \lambda = 2 - \frac{1}{2} \varepsilon + \left(\frac{1}{2} \alpha_0 E^2 - \frac{3}{8} \right) \varepsilon^2 + \dots. \quad (68)$$

Equation (63) tells us that

$$\begin{aligned} (-r_3^*) &= 1 - \frac{1}{\lambda} \left[\frac{1 + 2g'\frac{1}{\lambda} + \cdots}{1 + g'\frac{1}{\lambda} + \cdots} \right] = 1 - \frac{1}{\lambda} \left[1 + O\left(\frac{1}{\lambda^2}\right) \right] + \cdots \\ &= 1 - \frac{\varepsilon}{\varepsilon\lambda} + \cdots = 1 - \frac{\varepsilon}{2 - \frac{1}{2}\varepsilon} + \cdots = 1 - \frac{\varepsilon}{2} \left(1 + \frac{1}{4}\varepsilon \right) + \cdots. \end{aligned}$$

Combining this result with (68), we conclude that

$$\begin{aligned} \alpha^* &= \frac{1}{\varepsilon} \cdot \frac{\varepsilon\lambda}{(-r_3^*)} = \frac{1}{\varepsilon} \cdot \frac{2 - \frac{1}{2}\varepsilon + \left(\frac{1}{2}\alpha_0 E^2 - \frac{3}{8}\right)\varepsilon^2 + \cdots}{1 - \frac{\varepsilon}{2} \left(1 + \frac{1}{4}\varepsilon \right) + \cdots} \\ &= \frac{1}{\varepsilon} \left[2 - \frac{1}{2}\varepsilon + \left(\frac{1}{2}\alpha_0 E^2 - \frac{3}{8}\right)\varepsilon^2 + \cdots \right] \cdot \left[1 + \frac{\varepsilon}{2} + \frac{3}{8}\varepsilon^2 + \cdots \right] \\ &= \frac{1}{\varepsilon} \cdot \left[2 + \frac{1}{2}\varepsilon + \left(\frac{1}{2}\alpha_0 E^2 + \frac{1}{8}\right)\varepsilon^2 + \cdots \right]. \end{aligned}$$

□

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E-mail address: hzhou@nps.edu

E-mail address: hongwang@ams.ucsc.edu

E-mail address: wang@math.fsu.edu